

Docket No.: 008312-030696.9

**IN THE UNITED STATES PATENT & TRADEMARK OFFICE**



IN RE APPLICATION OF: Sumio Ashida et al.

SERIAL NO: 10/717,963

FILED: November 21, 2003

FOR: PHASE-CHANGE OPTICAL RECORDING MEDIUM

**TRANSLATION OF DOCUMENT**

COMMISSIONER FOR PATENTS  
P.O. BOX 1450  
ALEXANDRIA, VA 22313-1450

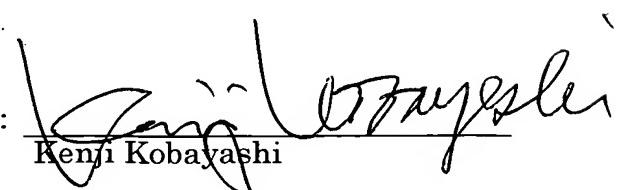
SIR:

Kenji Kobayashi, a translator residing at 2-46-10, Gokonishi,  
Matsudo-shi, Chiba-ken, Japan, hereby states:

- (1) that I know well both the Japanese and English languages;
- (2) that I translated the attached document identified as corresponding to Patent Application No. 2002-339437 filed in Japan on November 22, 2002 from Japanese to English;
- (3) that the attached English translation is a true and accurate translation to the best of my knowledge and belief.

DATE: August 9, 2006

BY:

  
Kenji Kobayashi

2002-339437

[Name of Document] PATENT APPLICATION  
[Reference Number] A000203596  
[Filing Date] November 22, 2002  
[To] Commissioner, Patent Office  
[International Patent Classification] G11B 7/24  
[Title of the Invention] PHASE-CHANGE OPTICAL RECORDING MEDIUM  
[Number of Claims] 6  
[Inventor]  
[Address or Residence] 1 Komukaitoshiba-cho, Saiwai-ku,  
Kawasaki-shi, Kanagawa  
c/o Corporate Research &  
Development Center of  
KABUSHIKI KAISHA TOSHIBA  
[Name] Sumio Ashida  
[Inventor]  
[Address or Residence] 1 Komukaitoshiba-cho, Saiwai-ku,  
Kawasaki-shi, Kanagawa  
c/o Corporate Research &  
Development Center of  
KABUSHIKI KAISHA TOSHIBA  
[Name] Keiichiro Yusu  
[Inventor]  
[Address or Residence] 1 Komukaitoshiba-cho, Saiwai-ku,  
Kawasaki-shi, Kanagawa  
c/o Corporate Research &  
Development Center of  
KABUSHIKI KAISHA TOSHIBA  
[Name] Takayuki Tsukamoto  
[Inventor]  
[Address or Residence] 1 Komukaitoshiba-cho, Saiwai-ku,  
Kawasaki-shi, Kanagawa  
c/o Corporate Research &  
Development Center of  
KABUSHIKI KAISHA TOSHIBA  
[Name] Katsutaro Ichihara

[Inventor]

[Address or Residence] 8 Shinsugita-cho, Isogo-ku,  
Yokohama-shi, Kanagawa  
c/o Yokohama Complex of  
KABUSHIKI KAISHA TOSHIBA

[Name] Noritake Ohmachi

[Inventor]

[Address or Residence] 8 Shinsugita-cho, Isogo-ku,  
Yokohama-shi, Kanagawa  
c/o Yokohama Complex of  
KABUSHIKI KAISHA TOSHIBA

[Name] Naomasa Nakamura

[Applicant for Patent]

[Identification Number] 00003078

[Name] KABUSHIKI KAISHA TOSHIBA

[Agent]

[Identification Number] 100058479

[Patent Attorney]

[Name] Takehiko Suzuye

[Phone Number] 03-3502-3181

[Appointed Agent]

[Identification Number] 100084618

[Patent Attorney]

[Name] Sadao Muramatsu

[Appointed Agent]

[Identification Number] 100068814

[Patent Attorney]

[Name] Atsushi Tsuboi

[Appointed Agent]

[Identification Number] 100092196

[Patent Attorney]

[Name] Yoshiro Hashimoto

[Appointed Agent]

[Identification Number] 100091351

[Patent Attorney]

[Name] Akira Kohno

[Appointed Agent]

[Identification Number] 100088683

[Patent Attorney]

[Name] Makoto Nakamura

[Appointed Agent]

[Identification Number] 100070437

[Patent Attorney]

[Name] Shoji Kawai

[Indication of Official Fee]

[Prepayment Register  
Number] 011567

[Amount of Payment] ¥21,000.-

[List of Items Submitted]

[Name of Item]	Specification	1
----------------	---------------	---

[Name of Item]	Drawings	1
----------------	----------	---

[Name of Item]	Abstract	1
----------------	----------	---

[Necessity of Proof] Necessary

[Document]

SPECIFICATION

[Title of the Invention] PHASE-CHANGE OPTICAL RECORDING MEDIUM

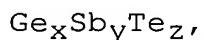
[What is claimed is:]

[Claim 1] A phase-change optical recording medium, characterized by comprising: a phase-change optical recording film that permits reversible phase change between a crystalline phase and an amorphous phase upon irradiation with light; and a film formed of hafnium oxide and in contact with at least one surface of the phase-change optical recording film.

[Claim 2] A phase-change optical recording medium, characterized by comprising: a plurality of phase-change optical recording films that permits reversible phase change between a crystalline phase and an amorphous phase upon irradiation with light on one surface thereof; and a film formed of hafnium oxide and in contact with at least one surface of at least one of the phase-change optical recording films.

[Claim 3] The phase-change optical recording medium according to claim 1 or 2, characterized in that the film formed of hafnium oxide contains hafnium oxide and at least one oxide selected from the group consisting of cerium oxide, titanium oxide and zirconium oxide.

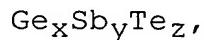
[Claim 4] The phase-change optical recording medium according to any one of claims 1 to 3, characterized in that the phase-change optical recording film is represented by the general formula:



where  $x+y+z = 100$ , and a composition thereof falls within

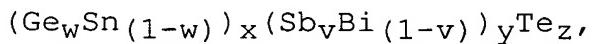
a range defined by  $x = 55$  and  $z = 45$ ;  $x = 45$  and  $z = 55$ ;  $x = 20$ ,  $y = 20$  and  $z = 60$ ; and  $x = 20$ ,  $y = 28$  and  $z = 52$  in the GeSbTe ternary phase diagram.

[Claim 5] The phase-change optical recording medium according to any one of claims 1 to 3, characterized in that the phase-change optical recording film is represented by the general formula:



where  $x+y+z = 100$ , and a composition thereof falls within a range defined by  $x = 55$  and  $z = 45$ ;  $x = 45$  and  $z = 55$ ;  $x = 25$ ,  $y = 16$  and  $z = 59$ ; and  $x = 25$ ,  $y = 24$  and  $z = 51$  in the GeSbTe ternary phase diagram.

[Claim 6] The phase-change optical recording medium according to claim 4 or 5, characterized in that the phase-change optical recording film is represented by the general formula in which at least one of Bi and/or Sn is substituted for a part of the constituent element of the phase-change optical recording film:



where  $x+y+z = 100$ ,  $0 \leq w < 0.5$ , and  $0 \leq v < 0.7$ .

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a phase-change optical recording medium in which phase change between a crystalline phase and an amorphous phase is reversibly caused by irradiation with a light beam so as to record information.

[0002]

[Prior Art]

(Principle of Phase-Change Optical Recording Medium)

The phase-change optical recording medium, comprising a phase-change optical recording film that permits reversible phase change between a crystalline phase and an amorphous phase upon irradiation with a light beam, is operated by the principle described in the following. In a write stage, a region irradiated with a light beam is heated to a temperature higher than the melting point thereof so as to be melted, followed by rapidly cooling the region to change the arrangement of the atoms in the region into an amorphous phase. In the erasing stage, a temperature in a region irradiated with a light beam is maintained for at least a prescribed period of time to fall within a temperature range from the crystallization temperature to the melting point. Then, where the initial state is crystalline, the crystalline phase is left unchanged. On the other hand, where the initial state is amorphous, the amorphous phase is crystallized. In a reading stage, utilizing the fact that the intensity of reflected light from the amorphous region differs from the intensity of reflected light from the crystalline region, the intensity changes of reflected light are converted into electric signals, and then the converted electric signals are subjected to analog-to-digital conversion so as to read out recorded information.

[0003]

Incidentally, it is also possible to carry out read/write

of information by utilizing a transition between a metastable crystalline phase such as a martensite phase and a stable crystalline phase or a transition between metastable crystalline phases, in addition to the phase change between the crystalline phase and the amorphous phase.

[0004]

(Approaches to Improve Recording Density)

For increasing an amount of information that can be recorded in a single recording medium, i.e., for increasing recording capacity, it is conceivable to improve recording density by the two methods given below.

[0005]

One method for improving the recording density is to reduce a pitch of the recording marks in the track direction. However, if the degree of size reduction proceeds, a region in which the pitch of the recording marks is made smaller than the size of the read beam is arrived at, with the result that it is possible for two recording marks to be included temporarily in the read beam spot. Where the recording marks are sufficiently apart from each other, the read signals can be greatly modulated so as to make it possible to obtain signals having high amplitude. However, where the recording marks are positioned close to each other, signals having low amplitude are obtained, with the result that errors tend to be generated when the obtained signals are converted into the digital data.

[0006]

The other method of improving the recording density is to reduce a track pitch. In this method, it is possible to

increase the recording density while avoiding significant influence given by degradation in signal intensity caused by the reduction in the mark pitch noted above. However, this method gives rise to a problem of a so-called "cross-erase" that, in a region in which the track pitch is substantially equal to or smaller than the size of the light beam, data on a certain track is degraded while the adjacent track is undergoing writing or erasing.

[0007]

The cross-erase is caused by the phenomenon that the recording mark is irradiated directly with the periphery of a laser beam on the adjacent track, and the phenomenon that the heat flow in the write stage flows into the adjacent track so as to elevate the mark temperature and, thus, to degrade the shape of the mark. It is necessary to overcome these problems for increasing the recording density of the phase-change optical recording medium.

[0008]

(Approach to Achieve High-Speed Recording)

High-speed recording is another requirement for the phase-change optical recording medium. For example, where video signals can be recorded in a time shorter than an actual viewing time, it is possible to realize easily a so-called "time-shift function" which is referred to as a function of viewing previous scenes in dubbing a distributed recording medium or in writing a broadcasting program. One of the factors for inhibiting the high-speed recording in the phase-change optical recording is the problem that the data fails to

be erased completely when the crystallization is performed by a laser beam having an erase level of a relatively low power in the overwriting stage, i.e., the problem of an insufficient erasure rate. Since a recording mark passes through a laser spot at high speed, the temperature of the recording mark fails to be maintained for a sufficiently long time to fall within a range within which crystallization can be achieved, with the result that the data fails to be erased completely.

[0009]

An idea of arranging a GeN-based interface film in contact with a phase-change optical recording film for accelerating crystallization so as to increase the erasure rate is disclosed in "Acceleration of crystallization process by nitride interface layer", Proceedings of the 10th Symposium on Phase Change Optical Information Storage, pp. 85-89. However, according to the experiments conducted by the present inventors, it has been found that, in the phase-change optical recording medium having a GeN-based interface film, a problem is generated in the write stage. The problem is based on the phenomenon that the peripheral portion of an initially melted region Im in the write stage is recrystallized, and an amorphous recording mark M is formed inside the recrystallized peripheral portion, as shown in FIG. 7. To be more specific, since it is necessary to melt a larger region in order to form a recording mark of a desired size, the cross-erase is to be promoted, with a reverse effect in view of high-density recording. On the other hand, if the writing is performed with a laser power that is allowable in terms of the

cross-erase, a problem is generated that the width of the recording mark to be formed is reduced so as to lower a carrier-to-noise ratio (CNR).

[0010]

Such being the situation, it has been desired to develop a novel material for the interface film, which permits increased crystallization speed in erasing so as to overcome the problem in terms of the insufficient erasure rate and which also makes it possible to suppress the recrystallization of the melted region in writing.

[0011]

(Increase in Recording Capacity by Dual-Layer Medium)

As another method for increasing the recording capacity, a method of superposing a plurality of information layers each containing a phase-change optical recording film is known. The particular method is disclosed in, for example, Jpn. Pat. Appln. KOKAI Publication No. 2000-322770. It should be noted that it is necessary for the first information layer positioned close to the light incident side to ensure at least about 50% of transmittance in order to prevent the light from being superfluously attenuated in accessing to the second information layer positioned remote from the light incident side. To this end, it is necessary to reduce the thickness of the recording film to about 5 to 7 nm. Since the thickness of the recording film is much reduced, the retention time required for the crystallization is made long, with the result that the recorded information fails to be erased completely in ordinary high-speed recording.

[0012]

As a measure for overcoming the difficulty, it is disclosed that a method of substituting Sn for a part of the GeSbTe recording film is effective, in Proceedings of the 12th Symposium on Phase-change Optical Information Storage PCOS 2000, pp. 36-41. Also, it is disclosed that a method of substituting Bi, In, Sn or Pb for a part of the GeSbTe recording film is effective, in Jpn. Pat. Appln. KOKAI Publication No. 2001-232941.

[0013]

However, for compensating the crystallization speed that has been lowered in accordance with the reduction in the thickness of the recording film, it is insufficient to substitute Sn for a part of the recording film material, and it is necessary to arrange a film producing the effect of accelerating crystallization at the interface with the recording film. According to the Proceedings of the 12th Symposium on Phase change Optical Information Storage, it is effective to arrange, for example, a GeN interface film. However, it has been found as a result of research conducted by the present inventors that, in the combination of a thin recording film having a thickness of about 5 to 7 nm and a conventional interface film such as the GeN film, the cross-erase is generated so that it is impossible to attain a sufficiently dense track pitch. On the other hand, it has been found that, in a medium in which no interface film is arranged, it is possible to suppress the recrystallization in a melted region allowing the cross-erase to be low, but the

erasure rate is pitifully insufficient.

[0014]

[Non-Pat. Document 1]

Proceedings of the 10th Symposium on Phase Change Optical Information Storage, pp. 85-89

[0015]

[Pat. Document 1]

Jpn. Pat. Appln. KOKAI Publication No. 2000-322770

[0016]

[Non-Pat. Document 2]

Proceedings of the 12th Symposium on Phase-change Optical Information Storage PCOS 2000, pp. 36-41

[0017]

[Pat. Document 2]

Jpn. Pat. Appln. KOKAI Publication No. 2001-232941

[0018]

[Object of the Invention]

An object of the present invention is to provide a phase-change optical recording medium, which scarcely allows recrystallization of a melted region in writing, thus lowering cross-erase, which makes it possible to ensure a sufficiently high CNR, and which also permits high-speed overwriting with a high recording density and a high capacity.

[0019]

[Means for Achieving the Object]

A phase-change optical recording medium according to an aspect of the present invention comprises: a phase-change optical recording film that permits reversible phase change

between a crystalline phase and an amorphous phase upon irradiation with light; and a film formed of hafnium oxide and in contact with at least one surface of the phase-change optical recording film.

[0020]

A phase-change optical recording medium according to another aspect of the present invention comprises: a plurality of phase-change optical recording films that permits reversible phase change between a crystalline phase and an amorphous phase upon irradiation with light on one surface thereof; and a film formed of hafnium oxide and in contact with at least one surface of at least one of the phase-change optical recording films.

[0021]

[Embodiments of the Invention]

The phase-change optical recording medium according to the embodiments of the present invention will now be described more in detail. The phase-change optical recording medium according to the embodiments of the present invention includes an interface film formed on at least one surface of the phase-change optical recording film and containing hafnium oxide. Incidentally, the expression "formed in contact with the phase-change optical recording film" is used unless a film not containing hafnium oxide is formed intentionally between the phase-change optical recording film and the interface film. For example, even where a very thin oxide film having a thickness of 2 nm or less, which is naturally formed on the surface of the phase-change optical recording film during the

deposition process, has been detected by, for example, Auger analysis, the interface film is regarded as being formed in contact with the phase-change optical recording film.

[0022]

Since the phase-change optical recording medium according to the embodiments of the present invention has the interface film containing hafnium oxide formed in contact with a phase-change optical recording film, it is possible to make the size of an amorphous recording mark M substantially equal to the size of an initially melted region Im in the write stage, as shown in FIG. 6.

[0023]

FIG. 1 is a cross-sectional view showing a stacked structure of a phase-change optical recording medium according to one embodiment of the present invention. In the phase-change optical recording medium as shown in FIG. 1, a dielectric film 2a, an interface film 3a, a phase-change optical recording film 4, an interface film 3b, a dielectric film 2b and a reflection film 5 are stacked successively in the order mentioned on a substrate 1.

[0024]

Incidentally, FIG. 1 shows the basic structure of the phase-change optical recording medium of the present invention. However, the structure of the phase-change optical recording medium of the present invention is not limited to the structure shown in FIG. 1. For example, in the phase-change optical recording medium as shown in FIG. 1, the interface films 3a, 3b are formed in contact with the both surfaces of the

phase-change optical recording film 4. However, it suffices for the interface film to be formed in contact with at least one surface of the phase-change optical recording film 4. Also, it is possible to form another film between the dielectric film 2b and the reflection film 4 or to use a plurality of films for forming the reflection film 4. Further, various modifications are conceivable as described herein later in detail.

[0025]

The recording film 4 in the phase-change optical recording medium is irradiated with light passing through the substrate 1. In many cases, the phase-change optical recording medium is designed to permit the reflectance ( $R_a$ ) of the amorphous portion and the reflectance ( $R_c$ ) of the crystalline portion to have a relationship of  $R_a < R_c$ , however, it is possible to design the phase-change optical recording medium to have a relationship of  $R_a > R_c$ , as described herein later.

[0026]

Hafnium oxide contained in the interface film is expressed as  $HfO_2$  in terms of the stoichiometric composition. However, it suffices for the hafnium oxide used in the embodiments of the present invention to have a composition represented by the formula  $HfO_x$ , where  $1.8 \leq x \leq 2.2$ .

[0027]

The present inventors have conducted extensive research using known interface film materials effective for accelerating crystallization of the recording film such as germanium nitride (GeN), silicon carbide (Si-C) and silicon nitride (Si-N). It

has been found that there is a trade-off relationship that a CNR is lowered in the case of using a material having a high effect of accelerating the crystallization and a material that permits a high CNR is poor in the effect of accelerating the crystallization. On the other hand, it has been found that, in the case of using hafnium oxide for the interface film, it is possible to obtain a high CNR and a high effect of accelerating the crystallization.

[0028]

It has been found that the effect similar to that described above can also be obtained in the case of using a mixture comprising hafnium oxide and at least one oxide selected from the group consisting of cerium oxide ( $\text{CeO}_2$ ), titanium oxide ( $\text{TiO}_2$ ) and zirconium oxide ( $\text{ZrO}_2$ ) for the interface film. In the case of mixing hafnium oxide with an oxide of the divalent metal, it is possible to obtain a high CNR and a high effect of accelerating the crystallization. On the other hand, when it comes to the combination of hafnium oxide and an oxide of a pentavalent metal such as  $\text{Ta}_2\text{O}_5$  or  $\text{Nb}_2\text{O}_5$  or an oxide of a trivalent metal such as  $\text{Mo}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ , it is impossible to achieve both a high CNR and a high effect of accelerating the crystallization. The mechanism that the combination of hafnium oxide and an oxide of a divalent metal can produce the particularly prominent effects as described above has not yet been clarified sufficiently. However, the reason for the above result is probably due to the fact that the bonding between the divalent metal and oxygen is stronger than the bonding between the pentavalent metal or the trivalent

metal and oxygen.

[0029]

In the case of using an interface film formed of a mixture comprising hafnium oxide and at least one oxide selected from the group consisting of cerium oxide, titanium oxide and zirconium oxide, it is possible to control easily the refractive index and/or the heat conductivity characteristics of the interface film while maintaining a satisfactory function of accelerating the crystallization.

[0030]

The recording film included in the phase-change optical recording medium absorbs light so as to be heated, and the heat is transmitted through the upper and lower films so as to cause the recording film to be cooled. The degree of heating and cooling of the recording film is changed in accordance with not only factors such as a light output, a linear velocity of the recording medium, an irradiating time with light and a crystallization speed of the recording film but also heat conductivity characteristics of the films formed on the upper and lower sides of the recording film, which determines whether the recording film is rendered amorphous or crystalline. It follows that, in order to form satisfactory recording marks on the recording film and to obtain sufficient erasure characteristics of the recording film at a desired linear velocity, it is desirable to control appropriately the heat conductivity of each of the films formed on the upper and lower sides of the recording film.

[0031]

When it comes to the interface film formed of the oxide mixture referred to above, the refractive index and/or the heat conductivity characteristics can be controlled in accordance with the types and the mixing ratio of the oxide materials which are to be mixed, with the result that the design of the film construction of the recording medium can be markedly facilitated. As a result, it is possible to employ a stacked structure in which only the interface film is formed, omitting the dielectric film (also called a protective film or a transparent interference film) made of ZnS:SiO<sub>2</sub> (a mixture of ZnS and SiO<sub>2</sub>), although it has been considered to be indispensable in the conventional phase-change optical recording medium. In the phase-change optical recording medium having the particular stacked structure, it is possible to decrease the total number of films (or the number of deposition processes) by the number of the dielectric film to be omitted, which improves productivity.

[0032]

FIGS. 2 and 3 are cross-sectional views each showing a stacked structure of the phase-change optical recording medium according to another embodiment of the present invention. In each of these phase-change optical recording media, at least one dielectric film is omitted from the stacked structure shown in FIG. 1.

[0033]

The phase-change optical recording medium shown in FIG. 2 has a structure that the dielectric film 2a, the interface film

3a, the phase-change optical recording film 4, the interface film 3b, and the reflection film 5 are stacked successively in the order mentioned on the substrate 1. That is, in the phase-change optical recording medium shown in FIG. 2, the dielectric film on the side of the reflection film relative to the recording film 4 is omitted from the stacked structure shown in FIG. 1.

[0034]

The phase-change optical recording medium shown in FIG. 3 has a structure that the interface film 3a, the recording film 4, the interface film 3b and the reflection film 5 are stacked successively in the order mentioned on the substrate 1. That is, in the phase-change optical recording medium shown in FIG. 3, the dielectric films on the light incident side and on the side of the reflection film relative to the recording film 4 are omitted from the stacked structure shown in FIG. 1.

[0035]

In the embodiments of the present invention, it is desirable to use, for example, GeSbTe for the phase-change optical recording film. In particular, a prominent effect can be obtained in the case of using the interface film specified in the present invention in combination with a GeSbTe phase-change optical recording film having a composition close to a so-called pseudo-binary system, which can be represented by  $(\text{GeTe})_a(\text{Sb}_2\text{Te}_3)_b$ , preferably a GeSbTe phase-change optical recording film having a composition close to the pseudo-binary system and containing Ge in an amount of at least 20 atomic %, and more preferably a GeSbTe phase-change optical recording

film having a composition close to the pseudo-binary system and containing Ge in an amount of at least 30 atomic %.

[0036]

To be more specific, when a material used for the phase-change optical recording film is represented by the general formula  $Ge_xSb_yTe_z$ , where  $x+y+z = 100$ , it is desirable to use a composition falling within a range defined by  $x = 55$  and  $z = 45$ ;  $x = 45$  and  $z = 55$ ;  $x = 20$ ,  $y = 20$  and  $z = 60$ ; and  $x = 20$ ,  $y = 28$  and  $z = 52$  in the GeSbTe ternary phase diagram.

[0037]

It is more desirable to use a composition falling within a range defined by  $x = 55$  and  $z = 45$ ;  $x = 45$  and  $z = 55$ ;  $x = 25$ ,  $y = 16$  and  $z = 59$ ; and  $x = 25$ ,  $y = 24$  and  $z = 51$  in the GeSbTe ternary phase diagram.

[0038]

Also, for the phase-change optical recording film, it is possible to use a material having Bi and/or Sn substituted for a part of the GeSbTe material of the composition range described above. The material referred to above is represented by the general formula,  $(Ge_wSn_{(1-w)})_x(Sb_vBi_{(1-v)})_yTe_z$ , where  $x+y+z = 100$ ,  $0 \leq w < 0.5$  and  $0 \leq v < 0.7$ . If the substitution ratio  $w$  of Sn for Ge is not lower than 0.5, the crystallization speed is rendered excessively high so as to cause the recrystallization after melting to be prominent, resulting in failure to form amorphous marks stably. Also, if the substitution ratio  $v$  of Bi for Sb is not lower than 0.7, the crystallization speed is also rendered excessively high so as to cause the recrystallization after melting to be prominent,

resulting in failure to form amorphous marks stably.

[0039]

Further, it is possible to use a recording film material prepared by adding traces of elements, e.g., Co, V and Ag, other than Sn and Bi, to GeSbTe such that the effect of the present invention is not impaired.

[0040]

In the embodiments of the present invention, as a material for the dielectric film (a protective film or a transparent interference film), typically used is ZnS: SiO<sub>2</sub>. To be more specific, the material for the dielectric film may include, for example, AlN, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiO, Si-O-N, Si-N, Al-O-N, Si-C, TiO<sub>2</sub>, Ta-N, Ta<sub>2</sub>O<sub>5</sub>, Ta-O-N, Zn-O, ZnS, ZrO<sub>2</sub>, Zr-O-N, Zr-N, Cr-O, Mo-O, W-O, V-O, Nb-O, Ta-O, In-O, Cu-O, Sn-O and In-Sn-O.

[0041]

Also, it is possible to design a phase-change optical recording medium of a so-called "Low-to-High" polarity, in which the reflectance of the amorphous portion is higher than the reflectance of the crystalline portion, by allowing the dielectric film on the light incident side to be formed of a stacked structure consisting of a plurality of dielectric films. For example, it is possible to realize the Low-to-High polarity by allowing the dielectric film on the light incident side to be of a three-layered structure of ZnS:SiO<sub>2</sub>/SiO<sub>2</sub>/ZnS:SiO<sub>2</sub> or of a two-layered structure of ZnS:SiO<sub>2</sub>/SiO<sub>2</sub> and by designing appropriately the thickness of each film.

[0042]

The appropriate thickness of each layer included in the phase-change optical recording medium shown in each of FIGS. 1 to 3 will now be described.

[0043]

In order to design the phase-change optical recording medium shown in FIG. 1 such that the reflectance ( $R_a$ ) of the amorphous portion is rendered lower than the reflectance ( $R_c$ ) of the crystalline portion, it is desirable for the total thickness of the dielectric film 2a and the interface film 3a on the light incident side to fall within a range of between 30 nm and 200 nm, for the thickness of the phase-change optical recording film 4 to be 20 nm or less, for the total thickness of the interface film 3b and the dielectric film 2b on the side of the reflection film to be 5 nm or more, and for the thickness of the reflection film 5 to fall within a range of between 30 nm and 400 nm. If the thickness of the phase-change optical recording film 4 exceeds 20 nm, the cross-erase tends to take place easily.

[0044]

The thicknesses of the films described above can also be applied to the cases where the dielectric film is omitted from the stacked structure consisting of the dielectric film and the interface film into the interface film alone as shown in FIGS. 2 and 3. Where the dielectric film other than the interface film 3a is not formed on the light incident side, it is desirable for the interface film 3a to have a thickness falling within a range of between 30 nm and 200 nm. Where the

dielectric film is not formed on the side of the reflection film, it is desirable for the interface film 3b to have a thickness of 5 nm or more.

[0045]

Also, in the case of using a stack of a plurality of dielectric films for a phase-change optical recording medium of the Low-to-High polarity ( $R_a > R_c$ ) as described above, it is desirable to determine the thickness of each dielectric film in a manner to satisfy desired reflectance under the condition that the total thickness of the plural dielectric films and the interface film 3a to fall within a range of between 30 nm and 200 nm.

[0046]

It is possible for the phase-change optical recording medium according to another embodiment of the present invention to be a so-called dual-layer single-sided recording medium having two phase-change optical recording films capable of independently writing, erasing and reading data by irradiation with light incident on one side.

[0047]

FIG. 4 is a cross-sectional view showing the stacked structure of a phase-change optical recording medium (dual-layer single-sided recording medium) according to another embodiment of the present invention. The phase-change optical recording medium shown in FIG. 4 having a structure in which a substrate 1a having a first information layer 10a formed thereon and a substrate 1b having a second information layer 10b formed thereon face each other and are bonded with the UV

resin adhesive 11 interposed between them. It is possible to employ the stacked structure as shown in, for example, FIGS. 1 to 3 for each of the first and second information layers 10a and 10b. Incidentally, prominent effects can be obtained by simply arranging the interface film in contact with the recording film included in the first information layer 10a positioned on the light incident side.

[0048]

It is to be noted that, in this phase-change optical recording medium, the light transmitting through the substrate 1a writes, erases and reads the first information layer 10a, and further the light transmitting through the first information layer 10a writes, erases and reads the second information layer 10b. For this reason, it is preferable for the first information layer 10a to be totally semi-transparent having a sufficient transmittance (about 50%).

[0049]

As described above, in order to increase the transmittance of the first information layer 10a, it is effective to decrease the thickness of each of the recording film and the reflection film. If the thickness of each of these films is decreased, however, the cooling effect is lowered. As a result, recrystallization of the melted region is rendered prominent in writing so as to give rise possibly to the inconvenience that it is difficult to perform the writing at an ordinary linear velocity. Such being the situation, for the first information layer 10a, it is desirable to employ the stacked structure capable of making up for the decrease of the

cooling effect.

[0050]

FIG. 5 shows an example of a stacked structure of a phase-change optical recording medium (a first information layer) according to another embodiment of the present invention. The phase-change optical recording medium shown in FIG. 5 has a structure that the dielectric film 2a, the interface film 3a, the phase-change optical recording film 4, the interface film 3b, a cooling interference film 6a the reflection film 5 and a cooling auxiliary film 6b are stacked successively in the order mentioned on the substrate 1a. One of the cooling interference film 6a and the cooling auxiliary film 6b may be omitted. In this recording medium, the region between the interface film 3b and the reflection film is configured by a film having a high cooling effect. It is also possible to insert a film having a low cooling effect (low heat conductivity), for example, ZnS:SiO<sub>2</sub>, between the interface film and the cooling interference film.

[0051]

The cooling interference film 6a formed between the interface film 3b and the reflection film 5 is made of a material having a heat conductivity higher than that of ZnS:SiO<sub>2</sub>, which is a dielectric film normally used. To be more specific, the material for the cooling interference film 6a includes: Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiO, Si-O-N, Si-N, Al-N, Al-O-N, Si-C, TiO<sub>2</sub>, Ta-N, Ta<sub>2</sub>O<sub>5</sub>, Ta-O-N, Zn-O, ZnS, ZrO<sub>2</sub>, Zr-O-N, Zr-N, Cr-O, Mo-O, W-O, V-O, Nb-O, Ta-O, In-O, Cu-O, Sn-O and In-Sn-O, and a mixture of these.

[0052]

The cooling auxiliary film 6b formed on the reflection film 5 functions as heat sink that compensates the decrease in cooling effect accompanied by the reduction in the thickness of the reflection film. To be more specific, the material for the cooling auxiliary film 6b includes a dielectric film having an appropriate heat conductivity: AlN, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiO, Si-O-N, Si-N, Al-O-N, Si-C, TiO<sub>2</sub>, Ta-N, Ta<sub>2</sub>O<sub>5</sub>, Ta-O-N, Zn-O, ZnS, ZrO<sub>2</sub>, Zr-O-N, Zr-N, Cr-O, Mo-O, W-O, V-O, Nb-O, Ta-O, In-O, Cu-O, Sn-O and In-Sn-O. In some cases, ZnS:SiO<sub>2</sub> may be used.

[0053]

In the phase-change optical recording medium (first information layer) shown in FIG. 5, it is desirable for the total thickness of the dielectric film 2a and the interface film 3a on the light incident side to fall within a range of between 30 nm and 200 nm, for the thickness of the phase-change optical recording film 4 to be 8 nm or less, for the total thickness of the interface film 3b and the cooling interference film 6a on the side of the reflection film to fall within a range of between 5 nm and 100 nm, for the thickness of the reflection film 5 to be 10 nm or less, and for the thickness of the cooling auxiliary film 6b to be 100 nm or less.

[0054]

In the first information layer of the dual-layer single-sided medium shown in FIG. 5, it is also possible to employ a stacked structure that a dielectric film (or a cooling interference film) is omitted as in FIGS. 2 and 3 relevant to

the stacked structure shown in FIG. 1. In this case, it is desirable for the interface film 3a on the light incident side to have a thickness falling within a range of between 30 nm and 200 nm and for the interface film 3b on the side of the reflection film to have a thickness falling within a range of between 5 nm and 30 nm.

[0055]

In the phase-change optical recording medium according to still another embodiment of the present invention, it is possible to bond a transparent sheet having a thickness of about 0.1 mm to the substrate, and by using an objective lens having a high NA of about 0.85, to irradiate the phase-change optical recording film with a light beam transmitted through the transparent sheet and the substrate.

[0056]

In the phase-change optical recording medium according to still another embodiment of the present invention, it is possible to bond a transparent sheet having a thickness of about 0.1 mm to the substrate, and by using an objective lens having a high NA of about 0.85, to irradiate the phase-change optical recording film with a light beam transmitted through the transparent sheet. In this case, in the medium in the example shown in, e.g., FIG. 1, the reflection film 5, the dielectric film 2b, the interface film 3b, the recording film 4, the interface film 3a and the dielectric film 2a are stacked successively in the order mentioned on the substrate, and finally the thin transparent sheet having a thickness of about 0.1 nm is formed. In the above particular structure, the

interface films are formed on both sides of the recording film. However, it is possible to omit either one of the interface films without deviating from the subject matter of the present invention. Also, it is possible to omit the dielectric film, as required, so as to form the interface film alone.

[0057]

Also in a medium of a type of accessing to a plurality of recording layers from one side, it is also possible to irradiate the recording films with a light beam transmitted through a thin transparent sheet having a thickness of about 0.1 mm, as described above. In this case, at least a metallic reflection film, a dielectric film, an interface film, a recording film, an interface film and a dielectric film are deposited successively in the order mentioned on the substrate having a thickness of about 1.1 mm. Then, a thin layer of ultraviolet curable resin having a suitable thickness of 10 nm to 50 nm is formed by spin-coating. Further, the resin is cured under the state that a stamper for forming a groove is pressed against the resin, followed by peeling off the stamper. Subsequently, a metallic reflection film, at least one dielectric film, the interface film, the recording film, the interface film and the dielectric film are deposited successively in the order mentioned on the substrate. Still further, a thin transparent sheet having a thickness of about 0.1 mm is bonded or a resin film having a thickness of about 0.1 mm is formed. In this fashion, it is possible to form a dual-layer recording medium conforming to a high NA of about 0.85. In the above particular structure, the interface films

are formed on both sides of the recording film. However, it is possible to omit either one of the interface films without deviating from the subject matter of the present invention. Also, it is possible to omit the dielectric film, as required, so as to form the interface film alone.

[0058]

Additionally, in the medium of a type accessing to a plurality of recording layers from one side and the medium (dual-layer single-sided optical recording medium) shown in FIG. 4, the metallic reflection film on the light incident side can also be omitted as required. In this case, for example, a design is preferably made to have refractive indices so as to obtain predetermined reflectance in interfaces between the thin films such as adhesive 11 and UV curable resin and the dielectric film in contact with them.

[0059]

[Examples]

Examples of the present invention will now be described.

[0060]

In each of the Examples, the phase-change optical recording medium was fabricated as follows. Specifically, a polycarbonate substrate having a thickness of 0.6 mm, formed by injection molding, was used as the substrate. Grooves were formed on the polycarbonate substrate at a pitch of 0.74  $\mu\text{m}$ . Therefore, in the case of land and groove recording, the track pitch comes to 0.37  $\mu\text{m}$ . Various films were successively deposited by sputtering on that surface of the polycarbonate substrate on which the grooves were formed. A so-called

cluster type sputtering apparatus, in which each film is deposited in a different chamber, was used. A target having a composition corresponding to that of the film to be deposited was mounted in each of the chambers. Since the sputtering apparatus was provided with a vacuum transfer chamber, the substrate was transferred under vacuum until deposition processes of all the films were completed.

[0061]

Further, the dual-layer single-sided optical recording medium was fabricated by bonding, with a UV resin, a pair of polycarbonate substrates deposition-processed as described above with their deposited surfaces inside.

[0062]

The phase-change optical recording medium thus obtained was mounted to an initializing apparatus so as to crystallize the recording film on the entire surface thereof. Then, the phase-change optical recording medium was evaluated by using a disk evaluating apparatus DDU-1000 manufactured by Pulstec Industrial Co., Ltd. The apparatus was equipped with a blue-violet semiconductor laser having a wavelength of 405 nm and an objective lens of NA 0.65. Experiments by the land and groove recording were carried out for the phase-change optical recording medium. Reflectance  $R_c$  of a crystalline portion and reflectance  $R_a$  of an amorphous portion were measured. Also, as will be described in the followings, an error rate of the data was evaluated by the bit error rate (BER) measurement, and read signal qualities were evaluated by analog measurements. A carrier-to-noise ratio (CNR), a DC erasure rate, and

cross-erase (X-E) were determined by the analog measurements. Each of the measurements was performed in respect of the tracks on the groove (G) and the land (L).

[0063]

In the land and groove recording, the track pitch becomes 0.37  $\mu\text{m}$  as described above. The linear velocity of the recording medium was set at 6.7 m/s. In the following description, the 2T mark has a mark length of 0.21  $\mu\text{m}$ , and the 9T mark has a mark length of 0.95  $\mu\text{m}$ .

[0064]

The BER measurement was carried out as follows. First, a mark train containing marks of 2T to 9T at random was overwritten 10 times in a target track. Then, the same random pattern was overwritten 10 times in each of the adjacent tracks on both sides of the target track, followed by measuring the BER on the target track.

[0065]

The analog measurements were carried out as follows. First, a mark train containing marks of 2T to 9T at random was overwritten 10 times in a target track. Then, a 9T mark train (single pattern) was overwritten once in the target track. The carrier-to-noise ratio (CNR) of the signal frequency of the 9T marks was measured with a spectrum analyzer. Then, the target track was irradiated with a laser beam at an erasing power level during one rotation of the disc as to erase the recording marks, followed by determining decrease in the signal level of the 9T marks. This is defined as a DC erasure rate. Also, the head was moved to a sufficiently remote track, and cross-erase

(X-E) measurement was carried out as follows. First, a 2T mark train was overwritten 10 times in a target track, followed by measuring the signal level of the 2T marks with a spectrum analyzer. Then, a 9T mark train was overwritten 10 times in each of the adjacent tracks on both sides of the target track. Thereafter, the head was brought back to the target track where the 2T mark train was written so as to measure again the signal level of the 2T marks. The decrease in the signal level of the 2T marks relative to the level measured first was defined as the cross-erase value.

[0066]

Examples A to F and Comparative Examples:

Phase-change optical recording media having various stacked structures were fabricated. Tables 1 to 3 show the structure of each of the phase-change optical recording media and the evaluation results.

[0067]

[Table 1]

	Example A	Comparative Example 1	Comparative Example 2	Comparative Example 3
Dielectric film 2a	ZnS:SiO <sub>2</sub> 50nm	ZnS:SiO <sub>2</sub> 50nm	ZnS:SiO <sub>2</sub> 50nm	ZnS:SiO <sub>2</sub> 53nm
Interface film 3a	HfO <sub>2</sub> 3nm	GeN 3nm	SiN 3nm	None
Recording film 4	Ge <sub>40</sub> Sb <sub>8</sub> Te <sub>52</sub> 13nm			
Interface film 3b	HfO <sub>2</sub> 3nm	GeN 3nm	SiN 3nm	None
Dielectric film 2b	ZnS:SiO <sub>2</sub> 15nm	ZnS:SiO <sub>2</sub> 15nm	ZnS:SiO <sub>2</sub> 15nm	ZnS:SiO <sub>2</sub> 18nm
Reflection film 5	Ag alloy 150nm	Ag alloy 150nm	Ag alloy 150nm	Ag alloy 150nm
Rc	19.2	18.6	18.4	19.3
Ra	2.4	2.2	2.1	2.3
BER (G)	1.40E-05	4.80E-04	9.20E-03	1E-02 or higher
BER (L)	1.25E-05	4.70E-04	7.60E-03	1E-02 or higher
CNR (G) [dB]	56.4	56.2	54.6	46.4
CNR (L) [dB]	56.2	55.8	53.8	45.8
Erasure rate (G) [dB]	-33.2	-30.2	-21.4	-2.4
Erasure rate (L) [dB]	-34.2	-31.2	-18.5	-1.5
X-E (G) [dB]	-0.2	-3.5	-1.2	0
X-E (L) [dB]	0	-0.7	-0.3	0

[Table 2]

	Example B	Example C	Example D1	Example D2	Comparative Example D
Dielectric film 2a	ZnS:SiO <sub>2</sub> 50nm	None	ZnS:SiO <sub>2</sub> 50nm	ZnS:SiO <sub>2</sub> 50nm	ZnS:SiO <sub>2</sub> 50nm
Interface film 3a	HfO <sub>2</sub> -CeO <sub>2</sub> 3nm	HfO <sub>2</sub> -ZrO <sub>2</sub> 55nm	HfO <sub>2</sub> 3nm	HfO <sub>2</sub> 3nm	GeN 3nm
Recording film 4	Ge <sub>40</sub> Sb <sub>8</sub> Te <sub>52</sub> 13nm	Ge <sub>40</sub> Sb <sub>8</sub> Te <sub>52</sub> 13nm	Ge <sub>31</sub> Sb <sub>15</sub> Te <sub>54</sub> 13nm	Ge <sub>22</sub> Sb <sub>22</sub> Te <sub>56</sub> 13nm	Ge <sub>22</sub> Sb <sub>22</sub> Te <sub>56</sub> 20nm
Interface film 3b	HfO <sub>2</sub> -CeO <sub>2</sub> 3nm	HfO <sub>2</sub> -ZrO <sub>2</sub> 20nm	HfO <sub>2</sub> 3nm	HfO <sub>2</sub> 3nm	GeN 3nm
Dielectric film 2b	ZnS:SiO <sub>2</sub> 15nm	None	ZnS:SiO <sub>2</sub> 15nm	ZnS:SiO <sub>2</sub> 15nm	ZnS:SiO <sub>2</sub> 15nm
Reflection film 5	Ag alloy 150nm	Ag alloy 150nm	Ag alloy 150nm	Ag alloy 150nm	Ag alloy 150nm
Rc	20.4	19.4	17.5	15.4	18.4
R <sub>a</sub>	1.9	1.6	1.9	2	3.5
BER (G)	2.20E-05	6.20E-06	2.00E-05	1.80E-05	1E-02 more
BER (L)	1.80E-05	4.20E-06	2.20E-05	2.10E-05	1E-02 more
CNR (G) [dB]	55.5	56.8	54.2	53.4	51.6
CNR (L) [dB]	56.2	55.2	53.6	52.8	50.5
Erasure rate (G) [dB]	-29.4	-28.5	-34.2	-37.2	-29.6
Erasure rate (L) [dB]	-30.1	-27.4	-35.3	-39.2	-30.4
X-E (G) [dB]	-0.3	-0.4	-0.5	-0.8	-6.8
X-E (L) [dB]	0	0	0	-0.3	-4.5

[0069]

[Table 3]

	Example E1	Example E2	Example F
Dielectric film 2a	ZnS:SiO <sub>2</sub> 50nm	ZnS:SiO <sub>2</sub> 50nm	ZnS:SiO <sub>2</sub> 50nm
Interface film 3a	HfO <sub>2</sub> 3nm	HfO <sub>2</sub> 3nm	HfO <sub>2</sub> 3nm
Recording film 4	Ge <sub>40</sub> Sb <sub>4</sub> Bi <sub>4</sub> Te <sub>52</sub> 10nm	Ge <sub>23</sub> Sn <sub>8</sub> Sb <sub>15</sub> Te <sub>54</sub> 10nm	Ge <sub>40</sub> Sb <sub>8</sub> Te <sub>52</sub> 20nm
Interface film 3b	HfO <sub>2</sub> 3nm	HfO <sub>2</sub> 3nm	HfO <sub>2</sub> 3nm
Dielectric film 2b	ZnS:SiO <sub>2</sub> 15nm	ZnS:SiO <sub>2</sub> 15nm	ZnS:SiO <sub>2</sub> 15nm
Reflection film 5	Ag alloy 150nm	Ag alloy 150nm	Ag alloy 150nm
Rc	19.1	18.2	21.5
Ra	2.2	2.1	2.2
BER (G)	2.40E-05	1.70E-05	3.20E-05
BER (L)	1.20E-05	9.00E-06	2.50E-05
CNR (G) [dB]	54.2	54.6	56.2
CNR (L) [dB]	53.8	53.2	56.3
Erasure rate (G) [dB]	-31	-32.2	-31.6
Erasure rate (L) [dB]	-30.5	-31.2	-30.2
X-E (G) [dB]	0	-0.2	-0.9
X-E (L) [dB]	0	0	-0.3

[0070]

Example A (HfO<sub>2</sub> Interface Film):

A phase-change optical recording medium (Example A) having the structure as shown in FIG. 1 was fabricated. The material used for each film and the thickness thereof were as follows:

Dielectric film 2a = ZnS:SiO<sub>2</sub> (50 nm);

Interface film 3a = HfO<sub>2</sub> (3 nm);

Recording film 4 = Ge<sub>40</sub>Sb<sub>8</sub>Te<sub>52</sub> (13 nm);

Interface film 3b = HfO<sub>2</sub> (3 nm)

Dielectric film 2b = ZnS:SiO<sub>2</sub> (15 nm);

Reflection film 4 = Ag alloy (150 nm).

[0071]

The recording medium of Example A exhibited a bit error rate (BER) lower than  $2 \times 10^{-5}$  for each of the land and the groove, which was permissible level for a practical use. The excellent BER is also supported by the excellent analog characteristics including CNR higher than 56 dB, the erasure rate lower than -29 dB and the cross-erase of -0.2 dB or less. In other words, a satisfactory BER can be obtained because the CNR is excellent and the cross-erase is low in the case of using HfO<sub>2</sub> for the interface film.

[0072]

Comparative Example A1 (GeN Interface Film) and Comparative Example A2 (Si-N Interface Film):

For comparison, phase-change optical recording media having the stacked structure equal to that of Example A were fabricated, except that GeN and Si-N were used for the

interface films in Comparative Examples A1 and A2, respectively.

[0073]

The recording medium of each of Comparative Examples A1 and A2 was found to be inferior in the BER compared to Example A by 1 to 2 digits. To be more specific, the medium of Comparative Example A1, in which the interface film was formed of GeN, was found to be poor in the BER because the cross-erase was likely to be generated easily. The recording medium of Comparative Example A2, in which the interface film was formed of Si-N, was found to be poor in the BER because the CNR was low.

[0074]

Incidentally, it is possible to improve either the CNR or the cross-erase to some extent by controlling the thickness of the interface film even in the case of using GeN or Si-N. However, it is impossible to improve simultaneously both the CNR and the cross-erase.

[0075]

Comparative Example A3 (No Interface Film):

For comparison, a phase-change optical recording medium (Comparative Example A3) having a stacked structure in which the interface films are omitted from the recording medium of Example A was fabricated.

[0076]

In the recording medium of Comparative A3, it was impossible to measure the BER. Also, in the recording medium of Comparative Example A3, the CNR value was also very small,

which reflects the poor erasure rate in overwriting. It follows that, in the recording medium of Comparative Example A3, it was substantially impossible to achieve rewriting under the evaluating conditions employed.

[0077]

Example B (Change in Composition of Interface Film):

A phase-change optical recording medium (Example B) having the stacked structure equal to that of Example A was fabricated, except that HfO<sub>2</sub>-CeO<sub>2</sub> (the molar ratio of 60:40) was used for the interface films in place of HfO<sub>2</sub>.

[0078]

The recording medium of Example B was somewhat inferior to the recording medium of Example A in respect of the cross-erase X-E, but was superior to the recording medium of Example A in each of the CNR and the erasure rate.

[0079]

Example C (Omission of Dielectric Film):

A phase-change optical recording medium (Example C) in which the dielectric films were omitted as shown in FIG. 3 and HfO<sub>2</sub>-ZrO<sub>2</sub> (the molar ratio of 40:60) is used for the interface films was fabricated. Incidentally, in accordance with omission of the dielectric films, the thickness of the interface film 3a on the light incident side was set at 55 nm, and the thickness of the interface film 3b on the side of the reflection film was set at 20 nm.

[0080]

The recording medium of Example C was found to be excellent in each of the cross-erase X-E, the CNR, and the

erasure rate. Also, since the total number of the films in the recording medium of Example C was smaller by two than that for Example A, it was possible to decrease the deposition processes, which brings about superior productivity.

[0081]

Where the dielectric films, which were widely used in the prior art, are omitted and the interface films alone specified in the present invention are formed in place of the dielectric films, it is desirable to pay sufficient attentions to the combination of the thickness and the heat conductivity of the interface film. To be more specific, if the interface film has excessively high heat conductivity, it is difficult to heat the recording film to reach the melting point thereof. On the other hand, if the heat conductivity of the interface film is excessively low, recrystallization in the melted region of the recording film is rendered prominent, with the result that decrease in the CNR and generation of the cross-erase X-E are promoted.

[0082]

In the recording medium of Example C,  $\text{HfO}_2\text{-ZrO}_2$  was used for the interface films, and the interface films formed on the light incident side and on the side of the reflection film relative to the recording film were made somewhat thicker so as to lead to the satisfactory results.

[0083]

Also, it is desirable to mix other elements and compounds containing other elements for controlling the heat conductivity. For example, it is possible to use a mixture of

HfO<sub>2</sub> and ZnS:SiO<sub>2</sub> for the interface film.

[0084]

Incidentally, in Example C, the dielectric films on the light incident side and on the side of the reflection film relative to the recording film are omitted. However, it is also possible to omit the dielectric film on the light incident side alone relative to the recording film as shown in FIG. 2. Also, it is possible to omit only the dielectric film on the side of the reflection film relative to the recording film.

[0085]

Examples D1, D2 and Comparative Example D (Influences Given by Composition of Recording Film):

A phase-change optical recording medium (Example D1) having the stacked structure equal to that of Example A was fabricated, except that the composition of the recording film was changed to Ge<sub>31</sub>Sb<sub>15</sub>Te<sub>54</sub> (Ge : Sb : Te = 4 : 2 : 7), lower in the Ge content than that for Example A.

[0086]

The recording medium of Example D1 was somewhat superior to the recording medium of Example A in the erasure rate, but was inferior in the CNR and the cross-erase X-E. However, a high cross-erase X-E as in Comparative Example A1 and a low erasure rate as in Comparative Example A2 were not observed in the recording medium of Example D1, supporting that the evaluation results for Example D1 were free from a practical problem. Therefore, it is believed that the effects due to the use of the HfO<sub>2</sub> interface film can be produced even in the case of changing the composition of the recording film.

[0087]

Also, a phase-change optical recording medium (Example D2) having the stacked structure equal to that of Example A was fabricated, except that the composition of the recording film was changed to Ge<sub>22</sub>Sb<sub>22</sub>Te<sub>56</sub>. It should be noted that the Ge content in the recording film for Example D2 is much lower than that in the recording film for Example D1.

[0088]

The recording medium of Example D2 exhibited a particularly excellent value in respect of the erasure rate, but was inferior to the recording medium of Example D1 in each of the CNR and the cross-erase X-E. However, a high cross-erase X-E as in Comparative Example A1 and a low erasure rate as in Comparative Example A2 were not observed in the recording medium of Example D2, supporting that the evaluation results for Example D2 were free from a practical problem.

[0089]

The reason why the recording medium of Example D2 is inferior to Example D1 in the CNR is that change in the optical characteristics (complex refractive indices n and k) between a crystalline phase and an amorphous phase is decreased with decrease in the Ge content of the recording film.

[0090]

In order to confirm the particular situation, a phase-change optical recording medium (Comparative Example D) having the stacked structure equal to that of Example D2 was fabricated, except that the interface film was changed to the conventional interface film made of GeN.

[0091]

In the recording medium of Comparative Example D, the CNR was further degraded to about 51 dB, compared with the recording medium of Example D2. Also, in the recording medium of Comparative Example D, the cross-erase X-E to the groove was high, i.e., -6.8 dB, and the cross-erase X-E to the land was much higher, i.e., -4.5 dB.

[0092]

Such being the situation, it has been confirmed that, in the case of using  $\text{HfO}_2$  for the interface films, the CNR can be increased and the cross-erase X-E can be lowered, compared with the case of using the conventional interface film, even if the recording film is formed of GeSbTe having a low Ge content.

[0093]

As described above, the interface film specified in the present invention permits prominent effects when used in combination with a GeSbTe recording film having a low Ge content, compared with the conventional interface film, and also permits further prominent effects when used in combination with a GeSbTe recording film having a higher Ge content.

[0094]

Examples E1 and E2 (Influences Produced by Composition of Recording Film, Substitution of Bi and Sn):

A phase-change optical recording medium (Example E1) having the stacked structure equal to that of Example A was fabricated, except that Bi was substituted partly for Sb contained in the material of the recording film such that the composition of the recording film was changed to  $\text{Ge}_{40}\text{Sb}_4\text{Bi}_4\text{Te}_{52}$

(Ge : Sb : Bi : Te = 10 : 1 : 1 : 13).

[0095]

The recording medium of Example E1 was somewhat inferior in the CNR to the recording medium of Comparative Example A1, but it was substantially free from the practical problem in the CNR value. The recording medium of Example E1 was superior in the erasure rate to the recording medium of Comparative Example A1, and thus it was free from the practical problem in the erasure rate. Also, the decrease in the signal level was not recognized at all in the recording medium of Example E1 even if the overwriting was performed 10 times on the adjacent tracks, with the result that the cross-erase X-E was particularly low. Such being the situation, the CNR after recording of signals on the adjacent tracks was found to be larger than the CNR after recording similarly performed on the adjacent tracks in Example A1. Therefore, it is found that prominent effects can also be produced in the case where the HfO<sub>2</sub> interface film is used in combination with the GeSbBiTe recording film.

[0096]

A phase-change optical recording medium (Example E2) having the stacked structure equal to that of Example D2 was fabricated, except that Bi was substituted partly for Ge contained in the material of the recording film such that the composition of the recording film was changed to Ge<sub>23</sub>Sn<sub>8</sub>Sb<sub>15</sub>Te<sub>54</sub> (Ge : Sn : Sb : Te = 3 : 1 : 2 : 7).

[0097]

The recording medium of Example E1 was somewhat inferior in the CNR to the recording medium of Comparative Example A1

but substantially equal to the recording medium of Comparative Example 2, which was substantially free from the practical problem in the CNR. The recording medium of Example E1 was superior in the erasure rate to the recording medium of Comparative Example A1, and thus it was free from the practical problem in the erasure rate. Also, the recording medium of Example E1 was particularly low in the cross-erase X-E. Such being the situation, the CNR after recording of signals on the adjacent tracks was found to be larger than that in Example A1. Therefore, it is found that prominent effects can also be produced in the case where the HfO<sub>2</sub> interface film is used in combination with the GeSnSbTe recording film.

[0098]

Example F (Influence Given by Thickness of Recording Film):

A phase-change optical recording medium (Example F) having the stacked structure equal to that of Example A was fabricated, except that the thickness of the recording film was set at 20 nm.

[0099]

The recording medium of Example F was superior in the overall characteristics to recording medium of each of Comparative Examples A1 and A2. On the other hand, the recording medium of Example F was substantially compared with the recording medium of Example A in the CNR and the erasure rate, but it was inferior to the recording medium of Example A in the cross-erase X-E. Therefore, it is desirable that the thickness of the recording film be smaller than 20 nm.

[0100]

Examples G, H and Comparative Example:

Phase-change optical recording media each having Low-to-High polarity, in which the reflectance Ra of the amorphous portion is higher than the reflectance Rc of the crystalline portion, were fabricated. Table 4 shows the structure of each of the phase-change optical recording media and the evaluation results.

[0101]

[Table 4]

	Example G	Comparative Example G	Example H
Dielectric film 2a	ZnS:SiO <sub>2</sub> 30nm	ZnS:SiO <sub>2</sub> 30nm	ZnS:SiO <sub>2</sub> 30nm
	SiO <sub>2</sub> 90nm	SiO <sub>2</sub> 90nm	SiO <sub>2</sub> 90nm
	ZnS:SiO <sub>2</sub> 20nm	ZnS:SiO <sub>2</sub> 20nm	-
Interface film 3a	HfO <sub>2</sub> -ZrO <sub>2</sub> 3nm	GeN 3nm	HfO <sub>2</sub> -ZrO <sub>2</sub> 25nm
Recording film 4	Ge <sub>40</sub> Sb <sub>8</sub> Te <sub>52</sub> 13nm	Ge <sub>40</sub> Sn <sub>8</sub> Te <sub>52</sub> 13nm	Ge <sub>40</sub> Sb <sub>8</sub> Te <sub>52</sub> 13nm
Interface film 3b	HfO <sub>2</sub> -ZrO <sub>2</sub> 3nm	GeN 3nm	HfO <sub>2</sub> -ZrO <sub>2</sub> 23nm
Dielectric film 2b	ZnS:SiO <sub>2</sub> 20nm	ZnS:SiO <sub>2</sub> 20nm	None
Reflection film 5	Ag alloy 150nm	Ag alloy 150nm	Ag alloy 150nm
Rc	5.5	5.2	5.8
Ra	27.3	27.5	28.5
BER (G)	7.2E-06	4.5E-05	5.8E-06
BER (L)	5.6E-06	8.2E-05	6.2E-06
CNR (G) [dB]	58.9	54.3	58.2
CNR (L) [dB]	58.2	55.2	58.4
Erasure rate (G) [dB]	-33.3	-32.1	-33.8
Erasure rate (L) [dB]	-32.7	-31.8	-33.1
X-E (G) [dB]	-0.4	-4.2	-0.3
X-E (L) [dB]	-0.1	-1.5	0

[0102]

Example G (Low-to-High Recording medium using Dielectric Film of Three-Layer Structure):

A phase-change optical recording medium (Example G) having Low-to-High polarity was fabricated. The material used for each of the films and the thickness of each film are as follows:

Dielectric film 2a =

ZnS:SiO<sub>2</sub> (30 nm)/SiO<sub>2</sub> (90 nm)/ZnS:SiO<sub>2</sub> (20 nm);

Interface film 3a HfO<sub>2</sub>-ZrO<sub>2</sub> (3 nm);

Recording film 4 Ge<sub>40</sub>Sb<sub>8</sub>Te<sub>52</sub> (13 nm);

Interface film 3b HfO<sub>2</sub> (3 nm);

Dielectric film 2b ZnS:SiO<sub>2</sub> (20 nm);

Reflection film 4 Ag alloy (150 nm).

[0103]

In this phase-change optical recording medium, it was possible to achieve a large modulation degree such that the reflectance Ra of the amorphous portion was 27.3% and the reflectance Rc of the crystalline portion was 5.5%. Also, the recording medium was particularly excellent in the CNR and exhibited a very low in the BER because it was excellent in the erasure rate and the cross-erase X-E.

[0104]

Comparative Example G (GeN Interface Film):

For comparison, a phase-change optical recording medium (Comparative Example G) having the stacked structure equal to that of Example G was fabricated, except that GeN was used for the interface films.

[0105]

The recording medium of Comparative Example G was excellent in the reflectance difference like the recording medium of Example G, but it was inferior in the CNR. This is because the region that was once melted in the write stage was not entirely rendered amorphous and was partly recrystallized so that the poor CNR was brought about. In this connection, the recording medium of Comparative Example G was also inferior in the BER compared to the recording medium of Example G.

[0106]

Example H (Omission of Dielectric Films):

A phase-change optical recording medium (Example H) having the stacked structure equal to the recording medium of Example G was fabricated, except that ZnS:SiO<sub>2</sub> dielectric film positioned close to the recording film 4 was omitted. Incidentally, in accordance with omission of the dielectric films, the thickness of the interface film 3a on the light incident side was set at 25 nm, and the thickness of the interface film 3b on the side of the reflection film was set at 23 nm.

[0107]

The recording medium of Example H was found to be high in each of the CNR value and the erasure rate. In addition, the recording medium was excellent in productivity.

[0108]

Examples J and K and Comparative Examples:

Dual-layer single-sided optical recording media were fabricated. Table 5 shows the configuration of the first

information layer on the light incident side and evaluation results (FIG. 5 does not show the configuration and evaluation results of the second information layer)

[0109]

[Table 5]

	Example J	Comparative Example J	Example K
Dielectric film 2a	ZnS:SiO <sub>2</sub> 45nm	ZnS:SiO <sub>2</sub> 45nm	None
Interface film 3a	HfO <sub>2</sub> 3nm	GeN 3nm	HfO <sub>2</sub> -CeO <sub>2</sub> 40nm
Recording film 4	Ge <sub>40</sub> Sb <sub>4</sub> Bi <sub>4</sub> Te <sub>52</sub> 6nm	Ge <sub>40</sub> Sb <sub>4</sub> Bi <sub>4</sub> Te <sub>52</sub> 6nm	Ge <sub>40</sub> Sb <sub>4</sub> Bi <sub>4</sub> Te <sub>52</sub> 7nm
Interface film 3b	HfO <sub>2</sub> 3nm	GeN 3nm	HfO <sub>2</sub> -CeO <sub>2</sub> 12nm
Cooling interference film 6a	Al <sub>2</sub> O <sub>3</sub> 10nm	Al <sub>2</sub> O <sub>3</sub> 10nm	None
Reflection film 5	Ag alloy 5nm	Ag alloy 5nm	Ag alloy 5nm
Cooling auxiliary film 6b	AlN 20nm	AlN 20nm	AlN 20nm
Rc	9.2	9.5	11.2
Ra	2.4	2.5	2.1
BER (G)	3.8E-05	7.5E-04	2.1E-05
BER (L)	3.2E-05	6.8E-04	2.4E-05
CNR (G) [dB]	52.4	50.2	53.4
CNR (L) [dB]	51.8	49.8	54.2
Erasure rate (G) [dB]	28.4	27.6	29.3
Erasure rate (L) [dB]	27.6	27.2	30.9
X-E (G) [dB]	-0.1	-1.4	-0.2
X-E (L) [dB]	0	-0.5	0

[0110]

Example J (First Information Layer of Dual-layer Single-sided Optical Recording Medium):

The first information layer of the dual-layer single-sided optical recording medium (Example J) of this example has

the stacked structure as shown in FIG. 5. The Material used for each film deposited on the polycarbonate substrate having the thickness of 0.6 mm and the thickness thereof are as follows. This first information layer showed the transmittance of 50%.

Dielectric film 2a = ZnS:SiO<sub>2</sub> (45 nm);

Interface film 3a = HfO<sub>2</sub> (3 nm);

Recording film 4 = Ge<sub>40</sub>Sb<sub>4</sub>Bi<sub>4</sub>Te<sub>52</sub> (6 nm);

Interface film 3b = HfO<sub>2</sub> (3 nm)

Cooling interference film 6a = Al<sub>2</sub>O<sub>3</sub> (10 nm)

Reflection film 4 = Ag alloy (5 nm)

Cooling auxiliary film 6b = AlN (20 nm)

On the other hand, the second information layer was prepared by depositing Ag alloy, ZnS:SiO<sub>2</sub>, GeSbTe recording films and ZnS:SiO<sub>2</sub> on another polycarbonate substrate having a thickness of 0.6 mm.

[0111]

The pair of polycarbonate substrates described above are bonded with the UV resin adhesive with their deposited surface facing each other.

[0112]

The dual-layer single-sided optical recording medium thus prepared was set in an initializing apparatus, and the recording film of the first information layer was subjected to crystallization. Then, evaluation was performed by adjusting the pick-up head of the evaluation apparatus to be focused on the first information layer.

[0113]

As shown Table 5, the first information layer of Example J is inferior in the CNR as compared to that of a single-layer single-sided phase-change optical recording medium (for example, Example A). This is because the reflectance difference between the crystalline phase and the amorphous phase is smaller than that of a single layer medium since a high transmittance of about 50% is ensured. On the other hand, in the first information layer of Example J, there was no practical problem in the value of erasure rate and the cross-erase was low.

[0114]

Comparative Example J (GeN interface film):

For comparison, the first information layer (Comparative Example J) having the stacked structure equal to that of Example J was fabricated, except that GeN was used for the interface films.

[0115]

The first information layer of Comparative Example J is further inferior in the CNR than that of the first information layer of Example J. It was found that the recording marks are recrystallized in writing, followed by a decrease in pitch thereof as compared to the track width, which is derived from the fact that GeN was used for the interface films. There was no practical problem in erasure rate, but the cross-erase was large.

[0116]

Example K (Omission of Dielectric Film):

The first information layer (Example K) having the stacked structure equal to that of Example J was fabricated, except that the dielectric film 2a and cooling interference film 6a were omitted. A mixture of HfO<sub>2</sub>-CeO<sub>2</sub> (a molar ratio of 40 : 60) was used as the material of the interface films. The interface film having this composition is optimal in heat conductivity characteristics and refractive rate. In addition, the thickness of the interface film 3a on the light incident side was set at 40 nm, and the film thickness of the interface film 3b on the side of the reflection film was set at 12 nm.

[0117]

The first information layer of Example K is superior in the CNR, erasure rate and cross-erase X-E as compared to that of the first information layer of Comparative Example J. Since the deposition process of the dielectric film and cooling interference film is not necessary, superior productivity is brought about.

[0118]

As described above, the material of the interface film in contact with the recording film according to the present invention brings about the effect of improving the crystallization speed. In the case where the crystallization speed is excessively high, for example, the interface film may contain a compound such as an oxide other than hafnium oxide, cerium oxide, titanium oxide and zirconium oxide, a nitride, a carbide and a sulfide, or another element. In particular,

the interface film greatly affects not only the crystallization speed but also temperature hysteresis of the recording film. It follows that it is desirable to add another compound or element to the interface film for controlling the heat conductivity. The particular case is not deviated from the subject matter of the present invention.

[0119]

[Advantage of the Invention]

According to the invention as specifically described above, a phase-change optical recording medium can be provided which scarcely allows recrystallization of a melted region in writing, thus lowering cross-erase, which makes it possible to ensure a sufficiently high CNR, and which also permits high-speed overwriting with a high recording density and a high capacity.

[Brief Description of the Drawings]

[FIG. 1]

A cross-sectional view showing the stacked structure of a phase-change optical recording medium according to one embodiment of the present invention.

[FIG. 2]

A cross-sectional view showing the stacked structure of a phase-change optical recording medium according to another embodiment of the present invention.

[FIG. 3]

A cross-sectional view showing the stacked structure of a phase-change optical recording medium according to another embodiment of the present invention.

[FIG. 4]

A cross-sectional view showing the stacked structure of a dual-layer single-sided recording medium according to still another embodiment of the present invention.

[FIG. 5]

A cross-sectional view showing the stacked structure of a first information layer of a dual-layer single-sided recording medium according to still another embodiment of the present invention.

[FIG. 6]

A view showing an amorphous mark in a phase-change optical recording medium according to an embodiment of the present invention.

[FIG. 7]

A view showing an amorphous mark in a conventional phase-change optical recording medium.

[Explanation of Reference Symbols]

- 1, 1a, 1b ... Substrate,
- 2a, 2b ... Dielectric film,
- 3a, 3b ... Interface film,
- 4 ... Phase-change optical recording film,
- 5 ... Reflection film,
- 6a ... Cooling interference film,
- 6b ... Cooling auxiliary film,
- 10a ... First information layer,
- 10b ... Second information layer.

【書類名】

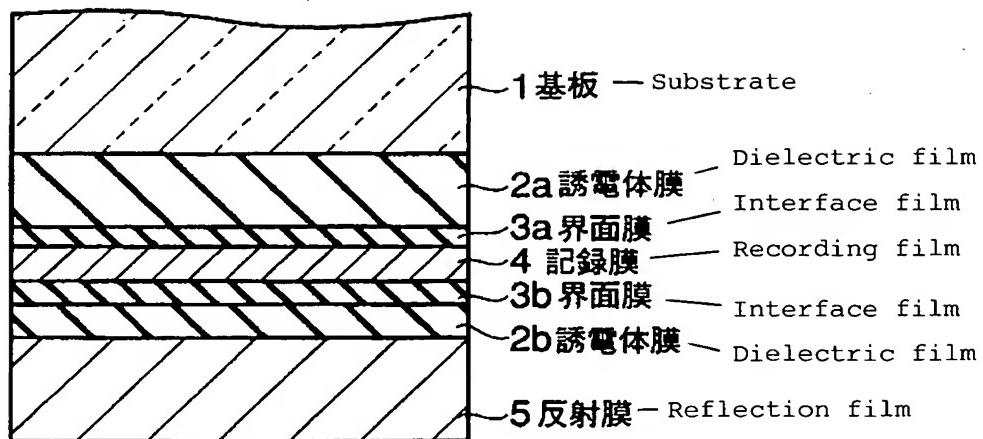
[NAME OF DOCUMENT]

【図1】

[FIG. 1]

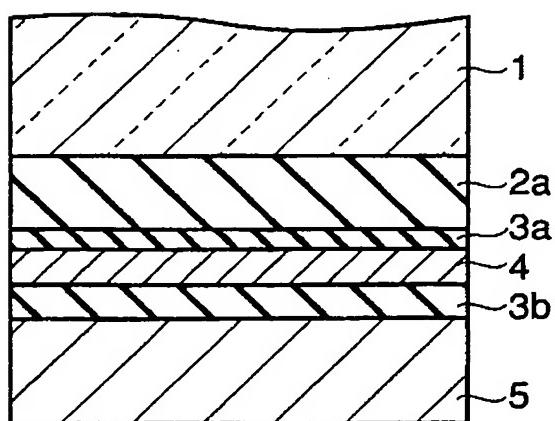
図面

DRAWINGS

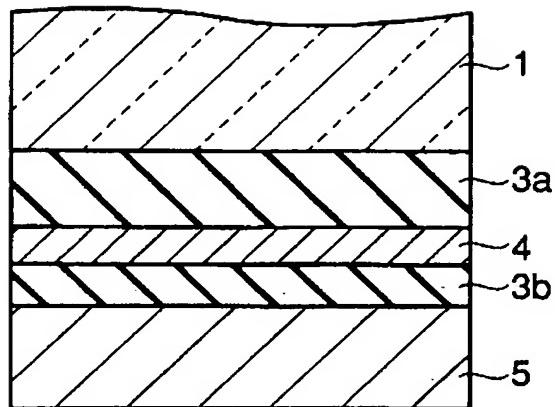


【図2】

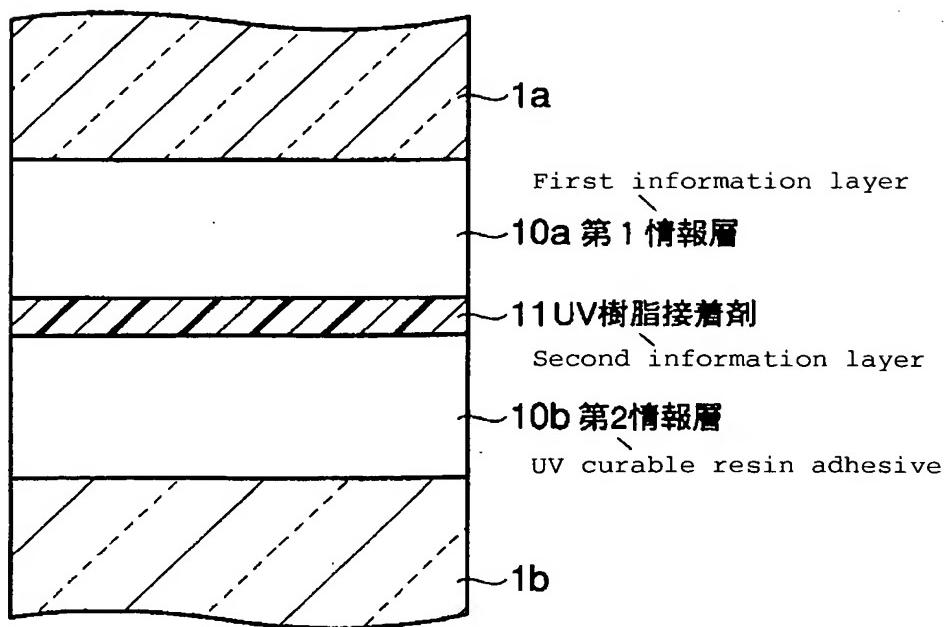
[FIG. 2]



【図3】  
[FIG. 3]

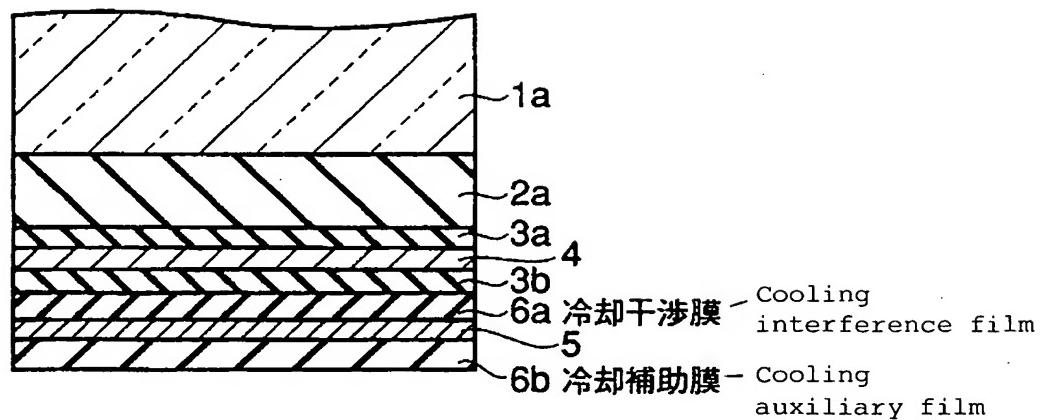


【図4】  
[FIG. 4]



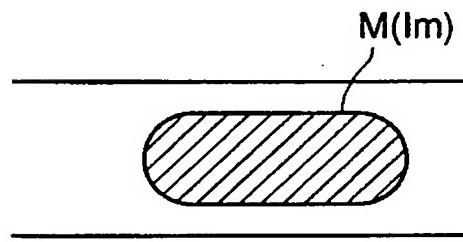
【図5】

[FIG. 5]



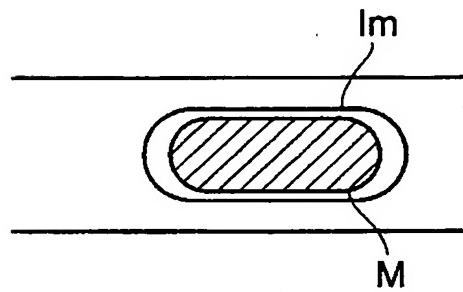
【図6】

[FIG. 6]



【図7】

[FIG. 7]



[Document]

## ABSTRACT

[Abstract]

[Object] To provide a phase-change optical recording medium, which scarcely allows recrystallization of a melted region in recording, thus lowering cross-erase, which makes it possible to ensure a sufficiently high CNR, and which also permits high-speed overwriting with a high recording density and a high capacity.

[Means for Achieving the Object] There is provided a phase-change optical recording medium, comprising: a phase-change optical recording film (4) that permits reversible phase change between a crystalline phase and an amorphous phase upon irradiation with light; and an interface film (3a, 3b) formed of hafnium oxide and in contact with at least one surface of the phase-change optical recording film (4).

[Elected Figure] FIG. 1